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(71) Applicant
Fuji Photo Film Co Ltd., (Japan), No 210 Nakanuma, Minami Ashigara-shi, Kanagawa, Japan.
(72) Inventor
Takayuki Hayashi
(74) Agent and/or Address for Service
Gee & Co., Chancery House, Chancery Lane, London WC2A 1QU.

(54) Heat sensitive recording paper

(57) Heat-sensitive recording paper comprises a paper support having thereon, in order, (a) a heat-sensitive color forming layer containing, usually in a binder, e.g. polyvinyl alcohol, (i) an almost colorless electron-donating color former, e.g. a triarylmethane, (ii) a phenol derivative or aromatic carboxylic acid capable of forming color when contacted with the color former, and (iii) 0.5 to 10.0 g/m^2 of MgO, CaO or Al_2O_3 as basic pigment, and (b) a top layer containing 2 to 4 g/m^2 of 80 to 100 mol% saponified polyvinyl alcohol and 1 to 20 parts of boric acid per 100 parts of the PVA.

The layer (a) may also contain oil-absorbing pigment, e.g. kaolin, or a wax or metallic soap.

The material is useful in facsimile recording machines.

The pigment keeps the surface of the color forming layer at pH of 6 or more so as to allow good bonding of the PVA and boric acid so that the top layer does not become sticky when wet.

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SPECIFICATION

Heat-sensitive recording paper

The present invention relates to a heat-sensitive recording paper and, particularly, to a heat-sensitive recording paper in which fading of color images and background fogging due to various chemicals and oils are prevented.

Heat-sensitive recording paper forms images by utilizing a physical or chemical change in a sensitive substance due to heat. A considerable number of such processes have been studied.

Recently, heat-sensitive recording papers have been used as output recording paper for facsimiles or output recording paper for computers. The paper is useful for such uses because primary color formation is directly carried out and a development step is not required. Such paper is called of the dye type, and has been described in Japanese Patent Publications 4160/68 and 14039/70 (U.S. Patents 2,663,654 and 2,967,785) and Japanese Patent Application (OPI) 27253/80 (U.S. Patent 4,283,458) (the term "OPI" as used herein refers to a published unexamined Japanese patent application).

Generally, when the heat-sensitive recording paper is used as recording paper, the recording apparatus can be made lighter in weight and smaller in size. Therefore, it has been increasingly utilized recently. On the other hand, heat-sensitive recording paper is not desirable because recorded images fade or become fogged when chemicals or oils adhere to it. Since this is an important problem in practical use, elimination of the problem has been desired.

In Japanese Utility Model Registration Application (OPI) 125354/81, it has been proposed that a top surface layer composed of a water-soluble high molecular compound is coated on the heat-sensitive color forming layer, to prevent permeation of plasticizers, by which an antifading property to plasticizers is improved. However, the resultant resistance to chemicals or oils is insufficient.

In Japanese Patent Application (OPI) 146794/81, it has been proposed that a surface layer containing a hydrophobic high molecular compound and/or a waterproofing agent in addition to a water-soluble high molecular compound is coated so as to give water resistance in addition to antifading property to plasticizers. In this proposal, an intermolecular cross-linking agent such as formaldehyde, glyoxal or melamine resin is used as the waterproofing agent. When the surface layer in which the water-soluble high molecular compound is subjected to intermolecular cross-linking is provided, resistance to various chemical and oils is improved as compared to the case of providing a surface layer composed of only the water-soluble high molecular compound, but the resistance is still not sufficient. Further, since the coated paper has a bad smell the unreacted formaldehyde remains on the coated paper, it is unpleasant to handle.

In order to improve the above-described disadvantages, it has been proposed in our U.K. Patent Application No. 8311227, Serial No. 2 119 531, having an earlier priority date than the present application, that a mixture of polyvinyl alcohol and boric acid be applied to a heat-sensitive color forming layer to form a surface layer. (The color forming layer may contain as oil absorbing pigment a kaolin, talc, pyrophyllite, diatomaceous earth, calcium, magnesium or barium carbonate, aluminum or magnesium hydroxide, titanium oxide or a urea-formaldehyde or cellulose filler; in the Examples calcium carbonate is present.) However, the top layer has somewhat insufficient resistance to water and it becomes sticky, causing adhesion of the heat-sensitive recording paper when water contacts the top surface layer.

This sticking phenomenon is not so much observed in the heat-sensitive recording paper having only a heat-sensitive color forming layer, because the heat-sensitive color forming layer permeates the paper support. However, with a material having the described separate top layer, which does not permeate the support due to the presence of the heat-sensitive color-forming layer, the sticking phenomenon easily occurs.

Accordingly, a primary object of the present invention is to provide a heat-sensitive recording paper having sufficient resistance to chemicals and oils, which is harmless with respect to pollution and has sufficient resistance to water.

According to the invention we provide a heat-sensitive recording paper comprising on a support a heat-sensitive color-forming layer containing an almost colorless electron-donating dye and an organic acid which forms a color on contact with said dye, as color-forming components; the color forming layer also contains an inorganic pigment, namely magnesium oxide, calcium oxide or aluminum oxide, which forms a basic color (blue) by Bromothymol Blue indicator; a top surface layer containing polyvinyl alcohol and boric acid is coated on said heat-sensitive color forming layer.

Boric acid is known to bond to polyvinyl alcohol by a monodiol type chemical bond, which is essentially different from intermolecular cross-linking agents such as formalin (formaldehyde), glyoxal or melamine resin.

The coating layer obtained by applying a mixture of polyvinyl alcohol and boric acid to the heat-sensitive col r forming layer shows a v ry desirable effect with resp ct to resistance to chemicals and oils. However, such a layer becomes sticky and can cause adhesion of the heat-sensitive recording paper when water sticks to the surface of the coating layer due to insufficient water resistance.

It is known that, if the mixture f polyvinyl alcohol and boric acid is kept at a pH 6.0 or more in order to solve the above-described fault, the bonds become strong and nhance water resistance.

However, if the mixture is kept at a pH 6.0 or more, it causes gelation of the solution and, consequently, it is impossible to apply.

Generally, aluminum salts such as aluminum sulfate, etc., are used as sizing assistants for paper. Accordingly, the surface pH f the pap r is 5.0 or less (the term: surface pH means pH of the surface of paper which is obtained by adding an indicator for measuring the pH of the surface of paper to the surface of paper and determining the pH of the surface of paper by measuring the degree of coloration, as shown in J. TAPPI, paper and pulp testing method No. 6-75). Generally, the coating solution for the heat-sensitive color-forming layer is alkaline. However, when it is applied to a paper support, the surface pH of the heat-sensitive color forming layer is reduced to 5.0 or less, because the volume of the paper layer is much larger than that of the heat-sensitive color forming layer (generally, by 5 to 20 times).

Therefore, even if a mixture of polyvinyl alcohol and boric acid is applied to the heat-sensitive color forming layer having a surface pH of 5.0 or less, water resistance is not improved because bonds between polyvinyl alcohol and boric acid are poor.

We have found that when one of said three selected inorganic pigments which form a basic color with Bromothymol Blue indicator is added to the heat-sensitive color forming layer to keep the surface pH of the heat-sensitive color forming layer at 6.0 or more, preferably 6.0 to 9.0, and a mixture of polyvinyl alcohol and boric acid is applied to the above-described layer, the bonds between the polyvinyl alcohol and boric acid are strengthened and the water resistance of the top layer formed is much improved.

Among known oil-absorbing pigments used for the heat-sensitive color forming layer, there are some basis pigments which form blue color with the Bromothymol Blue indicator. These pigments are generally added to the heat-sensitive color forming layer for the purpose of preventing pollution of the recording heat or reducing sticking. Accordingly, the purpose and the effect of their prior use are obviously different from in the present invention wherein a specific selected inorganic pigment is present in the color-forming layer so as to improve the water resistance of the layer of polyvinyl alcohol and boric acid.

The inorganic pigments which form a basic color (blue) with the Bromothymol Blue indicator in the heat-sensitive color forming layer are magnesium oxide, calcium oxide and aluminum oxide, preferably magnesium oxide. The preferred particle size of such inorganic pigments is 3 μ or less.

They may be added alone to the heat-sensitive color forming layer or together with conventional oil-absorbing pigments, by which it is possible to keep the surface pH of the heat-sensitive color forming layer at 6.0 or more.

The coating amount of the inorganic pigment used in the heat-sensitive color forming layer is preferably 0.5 to 10.0 g/m^2, more preferably 1.0 to 5.0 g/m^2.

If the amount is less than 0.5 g/m^2, the surface pH of the heat-sensitive color forming layer does not rise to 6.0 or more and, consequently, bonds between polyvinyl alcohol and boric acid become weak and deteriorate water resistance.

Further, if it is more than 10.0 g/m^2, color sensitivity of the heat-sensitive color forming layer deteriorates and desired density cannot be obtained.

Further, the saponification value of polyvinyl alcohol used in the coating solution is usually at least 80 by mol, preferably 90 to 100% by mol, and more preferably 98 to 100% by mol. If the saponification value of polyvinyl alcohol is lower than 80% by mol, resistance to chemicals and oils becomes insufficient. The polyvinyl alcohol used usually has a molecular weight of 500 to 1,700, preferably 900 to 1,700, and the polyvinyl alcohol is preferably applied in a coating amount of 2 to 4 g/m^2.

The amount of boric acid is usually 1 to 20 parts by weight, preferably 3 to 12 parts by weight, based on 100 parts by weight of polyvinyl alcohol. If the amount of boric acid is less than 1 part by weight, resistance to chemicals and oils becomes insufficient, and, if it is more than 20 parts by weight, application becomes difficult due to gelation.

The total coating amount of boric acid and polyvinyl alcohol is usually 1 to 10 g/m^2, preferably 3 to 5 g/m^2, as solid content.

A coating solution for the heat-sensitive color forming layer containing an inorganic pigment which forms a basic color (blue) with the Bromothymol Blue indicator in the above-described ratio and a coating solution for the coating layer composed of polyvinyl alcohol and boric acid are prepared. Then, the coating solution for the heat-sensitive color-forming layer is applied and dried. To the resulting layer, the coating solution for the coating layer is applied and dried to obtain the desired heat-sensitive recording paper.

Typical electron-donating colorless dyes (color former) used in the present invention include (1) triarylmethane compounds, (2) diphenylmethane compounds, (3) xanthene compounds, (4) thiazine compounds, and (5) spiropyran compounds. Examples of them include those described in U.S. Patent 4,283,458. The color former is preferably used in an amount of 0.3 to 1 g/m^2. Specific examples of triarylmethane compounds include 3,3-bis(*p*-dimethylaminophenyl)-6-dimethylaminophthalide (namely, Crystal Violet lactone), 3,3-bis (*p*-dimethylaminophenyl)phthalide, 3-(*p*-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-phenylindol-3-yl)phthalide, 3,3-bis(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-5-dimethylaminophthalid , 3,3-bis(2-phenylindol-3-yl)-5-dimethylaminophthalide and 3-p-dimethylaminophenyl-3-(1-methylpyrrol-2-yl)-6-dimethylaminophthalide. Specific examples of diphenylmethane compounds include 4,4'-bisdimethylaminobenzhydrin benzyl ether, N-halophenyl leuco Auramine

and N-2,4,5-trichlorophenyl leuco Auramine. Specific examples of xanthene compounds include Rhodamine B anilino lactam, Rhodamine (*p*-nitroanilino)lactam, Rhodamine B (*p*-chloroanilino)lactam, 7-dimethylamino-2-methoxyfluoran, 7-diethylamino-2-methoxyfluoran, 7-diethylamino-3-methoxyfluoran, 7-diethylamino-3-chloroflu ran, 7-diethylamino-3-chloro-2-methylfluoran, 7-diethylamino-2,3-dimethylfluoran, 7-diethylamino-(3-acetylmethylamino)fluoran, 7-diethylamino-(3-methylamino)fluoran, 3,7-diethylaminofluoran, 7-diethylamino-3-(dibenzylamino)fluoran, 7-diethylamino-3-(methylbenzylamino)fluoran, 7-diethylamino-3-(chloroethylmethylamino)fluoran and 7-diethylamino-3-(diethylamino)fluoran. Specific examples of thiazine compounds include benzoyl leuco Methylene Blue and *p*-nitrobenzyl leuco Methylene Blue. Specific examples of spiropyran compounds include 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3,3′-dichloro-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(3-methoxybenzo)spiropyran and 3-propyl-spiro-dibenzopyran. These compounds may be used alone or as a mixture. Xanthene type color formers are particularly preferred, because many of them generate less fogs and provide higher color densities.

Preferred organic acids used in the present invention include phenol derivatives and aromatic carboxylic acid derivatives, and bisphenols are particularly preferred. The organic acids are preferably used in an amount of 2 to 5 parts by weight per 1 part by weight of the color former. Examples of phenol derivatives include *p*-octylphenol, *p*-*tert*-butylphenol, *p*-phenylphenol, 1,1-bis(*p*-hydroxyphenyl)propane, 2,2-bis(*p*-hydroxyphenyl)propane, 1,1-*bis*(*p*-hydroxyphenyl)pentane, 1,1-*bis*(*p*-hydroxyphenyl)hexane, 2,2-*bis*(*p*-hydroxyphenyl)hexane, 1,1-*bis*(*p*-hydroxyphenyl)-2-ethyl-hexane and 2,2-*bis*(4-hydroxy-3,5-dichlorophenyl)propane, etc.

Examples of aromatic carboxylic acid derivatives include benzyl *p*-hydroxybenzoate, ethyl *p*-hydroxybenzoate, butyl *p*-hydroxybenzoate, 3,5-di-*tert*-butylsalicyclic acid, 3,5-di-α-methylbenzylsalicylic acid and polyvalent metal salts of the above-described carboxylic acids.

When producing a coating solution for the heat-sensitive recording paper, it is necessary to disperse the above-described materials for the heat-sensitive recording paper in water as a dispersion medium. In this case, it is preferred to use water-soluble high molecular compounds such as polyvinyl alcohol, hydroxyethyl cellulose or starch derivatives. In a process for dispersing the raw materials for the heat-sensitive recording material using such a dispersion medium, the electron donating dye or the organic acid is added in an amount of 10% by weight to 50% by weight (based on the weight of the dispersion solution) to the dispersi n medium containing generally 1% by weight to 10% by weight (based on the weight of the dispersion medium), preferably 2% by weight to 5% by weight of the water-soluble high molecular compound. Dispersion is carried out by means of a dispersing apparatus such as a ball mill, a sand mill, an attritor or a colloid mill.

To the above-described dispersion resulting from the mixing, the inorganic pigment which forms a basic color (blue) with the Bromothymol Blue indicator is added.

Further, oil-absorbing pigments, waxes, metal soaps and the like are added as occasion demands. The resulting coating solution for the heat-sensitive recording paper is applied to a base such as paper or plastic, etc., to obtain a desired heat-sensitive color forming layer.

Useful oil-absorbing pigments include kaolin, calcined kaolin, talc, agalmatolite, diatomaceous earth, calcium carbonate, titanium oxide, urea-formaldehyde filler and cellulose filler.

Useful waxes include paraffin wax, carnauba wax, microcrystalline wax, polyethylene wax and higher aliphatic acid amides such as stearic acid amide or ethylenebisstearoamide and higher aliphatic acid esters.

Useful metal soaps include higher aliphatic acid polyvalent metal salts, for example, zinc stearate, aluminum stearate, calcium stearate and zinc oleate.

The invention is illustrated by the following examples.

Example 1

20 g of 3-diethylamino-6-chloro-7-(β-ethoxyethyl(aminofluoran was dispersed by processing together with 100 g of a 10% aqueous solution of polyvinyl alcohol (saponification value: 98%, degree of polymerization: 500) in a 300 mℓ ball mill for 24 hours to obtain a dispersion (A). Likewise, 10 g of 2,2-bis(4-hydroxyphenyl)propane and 10 g of stearic acid amide were dispersed by processing together with 100 g of a 10% aqueous solution of polyvinyl alcohol in a ball mill for 24 hours to obtain a dispersion (B).

The dispersion (A) and the dispersion (B) were blended in a ratio by weight of 3:20. Further, to 200 g of the resulting mixture solution, 50 g of a fine magnesium oxide powder was added and dispersed sufficiently to prepare a coating solution for the heat-sensitive color forming layer.

This coating solution for the heat-sensitive color forming layer was applied to a base paper having an areal weight of 50 g/m^2 by an air knife so as to result in a coating amount of 6 g/m^2 as a solid content, and dried at 50°C for 2 minutes to form a heat-sensitive color forming layer.

When the surface pH of this heat-sensitive color forming layer was m asured, it was 7.6.

To this heat-sensitive color forming layer, a coating solution for the surface layer having the following composition was applied so as to result in a coated amount f 3 g/m^2 as solid content, and dried at 50°C for 2 minutes to form a surface layer. Thus, a heat-sensitive recording paper of the present invention was obtained.

Coating Solution for the Coating Layer:

5% Aqueous solution of polyvinyl alcohol (saponification value: 98%, degree of polymerization: 1,700)	100g
3% Aqueous solution of boric acid	10 g

Example 2

A heat-sensitive color forming layer was formed as in Example 1, except that 30 g of a fine magnesium oxide powder and 20 g of calcined kaolin which was a conventional oil-absorbing pigment were added instead of 50 g of the fine magnesium oxide powder.

The surface pH of this heat-sensitive color forming layer was 6.8.

A surface layer was formed as in Example 1.

Comparative Example 1

A heat-sensitive color forming layer was formed as in Example 1, except that calcined kaolin was added in the same amount as in Example 1 instead of the fine magnesium oxide powder.

When the surface pH of this heat-sensitive color forming layer was measured, it was 4.8.

A surface layer was formed as in Example 1 to obtain a comparative heat-sensitive recording paper.

Comparative Example 2

A heat-sensitive color forming layer was formed as in Comparative Example 1. A comparative heat-sensitive recording paper which did not have a surface layer was obtained.

Comparison Test:

Comparison tests of the heat-sensitive recording papers obtained in the Examples and Comparative Examples were carried out as follows.

(1) Fog and Color Formation Property:

The recording element was developed by applying an energy of 2 ms/dot and 50 mJ/m^2 at a density of 5 dots/mm in the chief scan and 6 dots/mm in the subscan to form a color on the heat-sensitive recording paper, and the fog density (density of the background before recording) and the color density after recorded (initial density) were measured by a reflection densitometer: Macbeth RD-514 (using a visual filter).

(2) Water Resistance of the Coating Film:

On the surface layer of the heat-sensitive recording layer (or on the heat-sensitive color forming layer in case that the sample had no surface layer), a drop of water was placed, and an organoleptic test of stickiness was carried out by softly rubbing the wet area with a finger.

(3) Resistance to Chemicals and Oils:

To the developed material obtained by the color formation test, various chemicals and oils were applied so as to have a thickness of about 0.5 μm. After being allowed to stand at 25°C in an atmosphere of RH 65% for 24 hours, the fog density (density of the background) and the color density were measured.

Results of the comparison tests are shown in Table 1.

Table 1 shows that there is no difference between the initial density in the Examples and that in the Comparative Examples. However, the water resistance in Comparative Example 1 is inferior and causes stickiness.

Further, though the stickiness is not caused in Comparative Example 2, its resistance to chemicals and oils is inferior. Further, increase of fog and deterioration of color density are observed.

On the contrary, the stickiness is not caused in the Examples and the resistance to chemicals and oils is remarkably good as compared with Comparative Example 1 and Comparative Example 2 which has no surface layer.

TABLE 1

Sample of Heat-Sensitive Recording Paper	Initial Density		Water Resistance	Resistance to Chemicals and Oils					
				Ethanol		Di-n-Butyl Phthalate		Castor Oil	
	Fog	Color Density		Fog	Color Density	Fog	Color Density	Fog	Color Density
Example 1	0.08	1.20	Not sticking	0.09	1.18	0.08	1.10	0.09	1.17
Example 2	0.08	1.20	Not sticking	0.10	1.19	0.08	1.11	0.09	1.17
Comparative Example 1	0.08	1.20	Sticking	0.10	1.18	0.08	1.08	0.09	1.16
Comparative Example 2	0.08	1.20	Not sticking	0.60	1.10	0.08	0.52	0.20	0.72

CLAIMS

1. A heat-sensitive recording paper, comprising:

a support having c ated thereon:

a heat-sensitive color-forming layer containing, as color-forming components, an almost colorless electron-donating dye and an organic acid capable of forming a color upon contact with the dye, and also containing as inorganic pigment magnesium oxide, calcium oxide or aluminum oxide; and

a surface layer positioned on the heat-sensitive color-forming layer, the surface layer comprising polyvinyl alcohol and boric acid.

2. A heat-sensitive recording paper as claimed in Claim 1, wherein the heat-sensitive color-forming layer has a surface pH of 6.0 or more.

3. A heat-sensitive recording paper as claimed in Claim 2, wherein the surface pH is 6.0 to 9.0.

4. A heat-sensitive recording paper as claimed in Claim 1, 2 or 3, wherein the inorganic pigment is present in an amount of 0.5 to 10.0 grams per square metre of the layer.

5. A heat-sensitive recording paper as claimed in Claim 4, wherein said amount of pigment is 1.0 to 5.0 g/m^2.

6. A heat-sensitive recording paper as claimed in Claim 1, wherein the polyvinyl alcohol has a saponification value of 80% by mol or more.

7. A heat-sensitive recording paper as claimed in Claim 6, wherein said saponification value is in the range of 90 to 100% by mol.

8. A heat-sensitive recording paper as claimed in Claim 7, wherein said saponification value is 98% to 100% by mol.

9. A heat-sensitive recording paper as claimed in any preceding claim, wherein the molecular weight of the polyvinyl alcohol is 500 to 1,700.

10. A heat-sensitive recording paper as claimed in Claim 9, wherein said molecular weight is 900 to 1,700.

11. A heat-sensitive recording paper as claimed in any preceding claim, wherein the polyvinyl alcohol is present in a coated amount of 2 to 4 g/m^2.

12. A heat-sensitive recording paper as claimed in any preceding claim, wherein the boric acid is present in an amount in the range of 1 to 20 parts by weight per 100 parts by weight of the polyvinyl alcohol.

13. A heat-sensitive recording paper as claimed in Claim 12, wherein said amount is in the range of 3 to 12 parts by weight per 100 parts by weight of the polyvinyl alcohol.

14. A heat-sensitive recording paper as claimed in any preceding claim, wherein the coated amount of boric acid and polyvinyl alcohol is in the range of 1 to 10 grams per square metre as the solid content.

15. A heat-sensitive recording paper as claimed in Claim 14, wherein the coated amount is in the range of 3 to 5 g/m^2.

16. A heat-sensitive recording paper, substantially as hereinbefore described in Example 1 or 2.

17. A colored image formed by imagewise local heating of a recording paper as claimed in any preceding claim.

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